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19th century wooden ship sheathing. A case of study: the materials of Puerto Pirámides 1, Península Valdés

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Abstract

Copper alloy sheathing used to protect ships hulls from different wood-infesting organisms (borers and foulers) was widespread since the late 18th century. In this work the characterization results of a sheathing fragment and tacks from the site *Puerto Pirámides 1*, Peninsula Valdes (Chubut Province, Argentina) are presented. Through metallographic analysis by means of Light Microscopy and Scanning Electron Microscopy (SEM), and chemical composition determination by Energy Dispersive X-ray Spectrometry (EDS) it was possible to identify compositions and microstructures different from those of artefacts of similar kind found in shipwrecks of the same period.

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Keywords: Copper-alloy sheathing, Archaeometallurgy, 19th century shipwreck

Introduction

For centuries, the action of aquatic borers and foulers, wood-infesting organisms, represented a serious threat to ships operativity. Diverse methods were tested in order to mitigate these problems and protect the hulls, such as

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wooden and metal sheets. Within the latter, copper and its alloys reached special significance since the last half of the 18th century. Staniforth (1985); Bingeman et al. (2000). Since then, numerous innovations on materials and manufacturing methods were introduced, many of which are kept in patent registers. Jones (2004). In some cases, as will be seen below, they can be used to temporally adscribe the archaeological register.

The need for copper sheathing to protect an increasing number of ships demanded great quantities of sheets and fixation elements. History and archaeology have contributed to the deeper knowledge of this technology. It is worth mentioning the characterization studies of sheathing and fixation elements of diverse shipwrecks. Jones (2004); Ciarlo (2013). The results from the analyses of tacks from 18th and 19th century sites, in particular, indicate that these pieces were mostly made manually, by smelting and mold casting in copper or copper alloys – tin, zinc and other minoritarian elements were often used -. Sheets, on the other hand, were manufactured in copper or copper alloy- specially brass - by rolling.

In this article, the characterization results of the metallic sheathing from a wooden shipwreck found at Puerto Pirámides, Península Valdés (province of Chubut, Argentina) are presented. Archaeological action was taken at the site in 2013, within the project "Relevamiento del Patrimonio Cultural Subacuático de Puerto Madryn y Península Valdés", from the Instituto Nacional de Antropología y Pensamiento Latinoamericano (INAPL) and under the direction of Dr. Dolores Elkin (CONICET-INAPL). The specific action at the shipwreck, named Puerto Pirámides 1 (PP1 from here on), was directed by Dr. Mónica Grosso together with architect Cristian Murray (INAPL).

2. Experimental Procedure

In the first instance, a superficial study was conducted to describe the macroscopic features and dimensions of the pieces. In the case of the sheet, scanning electron microscopy (SEM) was also applied. Metallography was used to carry out the microstructural analysis on longitudinal sections of the tacks and different sections of the sheet. Images were obtained by light microscopy (LM) and SEM.

The elemental chemical composition of all samples was determined by X-Ray Energy Dispersive Spectrometry (EDS). In the case of the sheet, in a fragment that was additionally extracted and pickled the following elements were determined; sulfur (S), copper (Cu) and others - namely iron (Fe), zinc (Zn) and tin (Sn) using respectively; infrared absorption method under ASTM E 1019-2011, electrodeposition, and atomic absorption flame spectrophotometry.

3. Results and Discussion

3.1. Sheathing.

Fig. 1(a) illustrates the sheet, where four aligned holes can be observed, through which fastening tacks passed.

The average diameter of the holes is 12±2 mm and they are 55±5 mm distant from each other. In Fig. 1(b) one of them can be seen in detail. Both sides of the sheet are covered in dark corrosion products (blackish and green-turquoise coloration), of granular morphology, that in some areas flake off (Fig. 1c). The thickness of the sheet, including the products, is of between 0,9 and 1,2 mm.

Heavily corroded copper based alloys on maritime environments present a greenish patina on their surface, with a predominant presence of atacamite, similar to that present in the sheet under study. Schweitzer (2007). Furthermore, in some areas, SEM revealed corrosion products with the shape of faceted crystals (Fig. 2). The morphology of the crystals is similar to that studied by Stoffyn-Egli and collaborators in brasses exposed to maritime environments. Furthermore, these authors noted a crystal-looking Cu-Zn hydrated sulfate. Stoffyn-Egli (1998).The composition of the sample, previously pickled, analysed by the techniques quoted above, is of 60,8% Cu and 37,6% Zn, with small percentages of other elements, namely: 1,3% Pb; 0,7 % Sn; 0,6% Fe and 0,015% S (in weight). Two areas of the sheet, one pickled and unpickled the other, were analysed by EDS. In table 1, the average compositions obtained are shown, and in Fig. 3, the representative spectrums. According to the mentioned results, the sheet is made of a Cu-Zn alloy, with traces of Fe and S. This composition is similar to a 60/40 brass known as Muntz metal, for which George

F. Muntz received a patent in 1832. It is worth noting that its use for sheathing became widespread by the 1840´s (Jones, 2004).

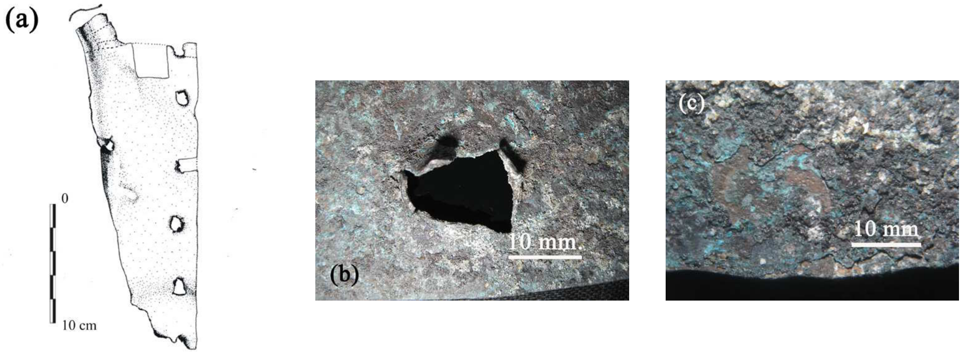

Figure 1 – Piece of Hull sheathing from the site PP1: a) illustration of the studied fragment; b) fastening hole; c) surface of the piece.

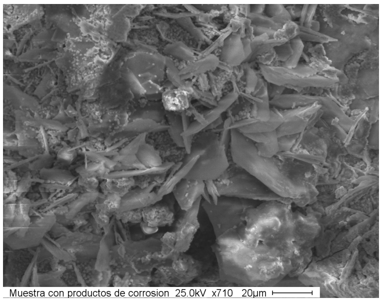

Figure 2 –SEM image of the faceted corrosion products.

Table 1 – Elemental composition of the sheet´s surface

Sheet	Elemental composition (in weight)							
	Cu	Zn	Fe	S	Mg	Si	Cl	Ca
pickled	65	36	0,6	0,5	-	-	-	-
Unpickled	34	48	0,7	6,8	1,3	2,3	6,4	1,8

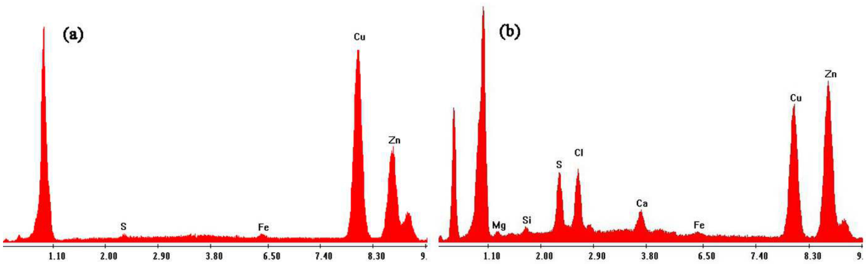

Figure 3 – EDS spectrums, representative of the following areas: a) pickled(using oxalic acid); b)unpickled.

The unpickled sample presented higher quantities of Zn, less Cu and similar amounts of Fe than the pickled one. Furthermore, a rise in S proportion could also be detected, as well as the presence of Si, Cl, Ca and Mg, elements associated to corrosion processes.

A sample for microstructural analysis was extracted from the sheet. It was pickled and mounted in Bakelite. The thickness, measured in this specimen, is of 0.41±0.07 mm. The surface of the sheet is corroded, and exhibits slight traces of dezincification, perceptible because of their reddish color (Fig. 4). Towards the centre, on the other hand, evenly distributed micropores can be observed.

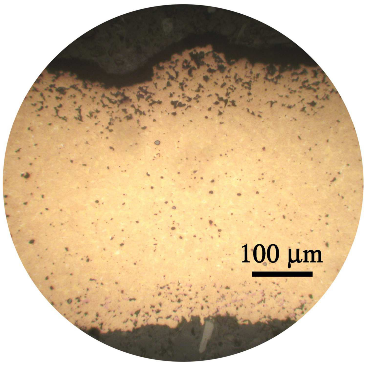

Figure 4 – Sheet section (polished, with no chemical etching) presenting evidence of degradation on the sheet`s edge

The microstructure and chemical composition mentioned correspond to an alpha-beta (α+β) brass of small equiaxed grains, with no plastic deformation (Fig. 5), with low β phase proportion (dark areas). The α phase grains present straight lines of annealing twins, that are typical of this kind of material. This microstructure is similar to the one registered in sheathing sheets found in other sites from the 19th century. Lorusso (2003). Furthermore, white areas and semispherical grey particles can be observed, mainly located at the grain boundaries of α phase and associated to β phase (Fig. 5b.)

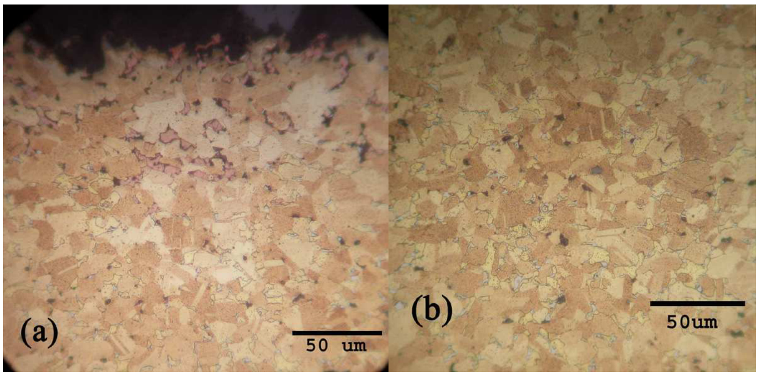

Figure 5 – Photomicrography of a section of the sheet: a) edge of the sample; b) center. Etchant: HCl $FeCl_3$ aqueous solution

The composition of the main phases and the quoted grey and white particles was obtained by EDS (Table 2). Taking into account the microstructures analyzed and the Zn equivalence coefficients proposed by Guillet and collaborators -Davies (1993)-, α phase is oversaturated of Zinc, while β phase presents a Zn composition close to the equilibrium condition. This is the phase with the greater Fe and Sn content. The grey particles seem to be Zn sulphur; while white ones, evenly distributed, correspond to a Cu-Sn compound.

Corrosion by dezincification, illustrated in Fig. 5, is typical of brasses exposed to salty environments (i.e. maritime) and its intensity varies according to the alloy composition and the β phase content. Davies (1993); Polan, (1992). Generally, a presence of Sn in percentages above 0,5% enhances the resistance to corrosion by dezincification. Polan (1992); Campanella et al. (2009). In this case, the presence of Sn can be considered either to have been caused by contamination during the manufacturing process or to have been added deliberately, foreseeing the sheet´s function.
Finally, a Vickers microhardness test was performed, from which a value of 120±10 HV was obtained. Similar values were reported on materials with a Zn content comparable to the one studied, as in 70/30 brasses that present deformation and subsequent heat treatment. Ozgowicz et al. (2010); Ashkenazi et al.(2014).

Table 2 – Phases and particles elemental composition: phase α, phase β, white particles, and grey particles

Zone	Elemental Composition (weight %)				
	Cu	Zn	Fe	Sn	S
Phase α	62	37			-
Phase β	55	43	1	1	-
White particles	53	36	2	9	-
Grey particles	8	60	-	-	32

3.2. Tacks

Fig. 6 illustrates the studied tacks. These have a square head 9±0,3 mm wide at the edge. In Table 3, their code, measures and general characteristics are depicted in detail.

Figure 6 – PP1 tacks: a) MT-1a; b) MT-1b.

Table 3 – Main characteristics of the studied tacks

Sample	Observations	Type of head and edge length (mm)	Length (mm)
MT-1a	Grey-greenish oxides cover the surface. No deformation in the body.	square 9±0,1	34±0,2
MT-1b	Grey-greenish oxides cover the surface. Deformation seen in the body (curved)	square 9±0,3	33,4±0,5

The surface of the pieces presents compact corrosion products similar to those observed on the sheet.

The average weight per cent composition of the tacks, analyzed via EDS in different areas, correspond to a biphasic brass α+β with 60,5% Cu, 39% Zn and Fe 0,7% (Fig. 7b). An alloy of similar composition was registered in two tack fragments from the same site. The presence of aligned nonmetallic particles, in which S and Zn are predominant (Fig. 7b) was detected at the head and shank of the MT-1a tack.

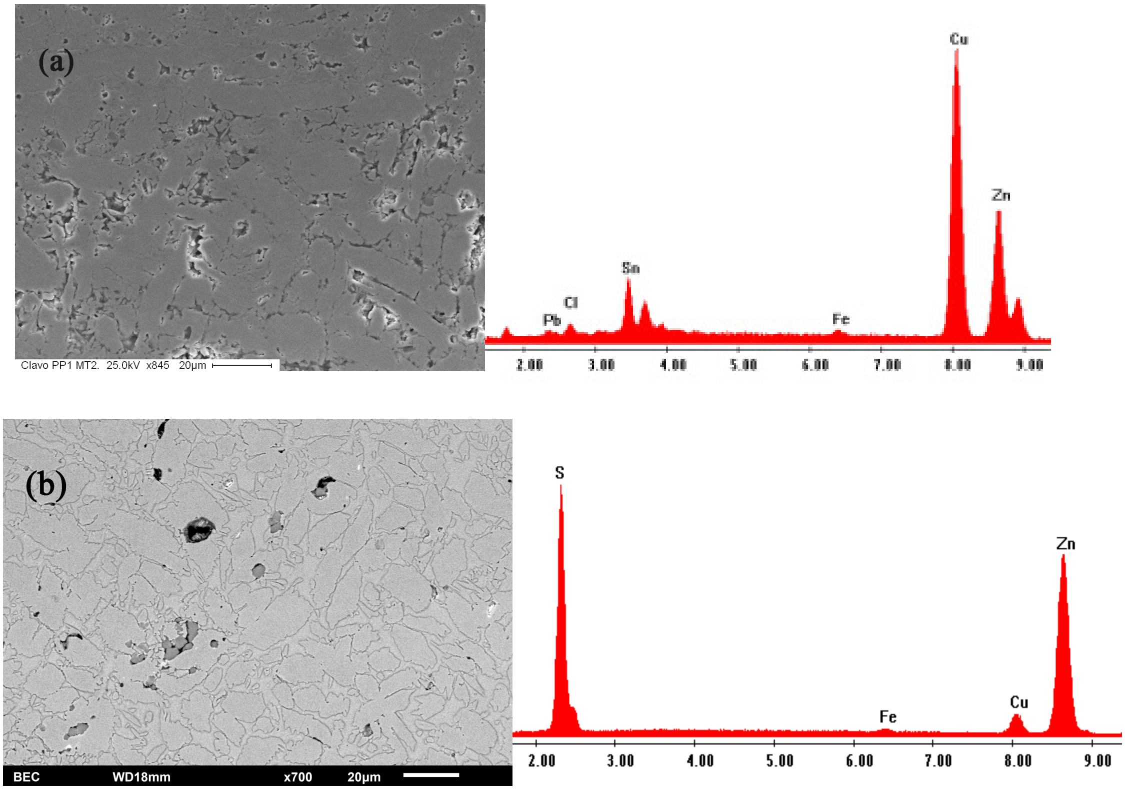

Figure 7 –SEM and EDS images of the MT-1a tack, corresponding to: a) The head-shank junction, a Sn-rich area; b) a string of sulphur precipitates in β phase.

In the previous sample, areas of a greater Sn concentration were observed at intergranular particles such as those close to the external surface of the head (Fig. 7a). The degradation process by dezincification reaches a depth of less than 0,5 mm. The change of the degraded area is clearly distinguished at a micrography of the shank´s edge (Fig. 8a). In Fig. 8(b), taken at the tip, areas of material where no corrosion exist.

The MT-1b tack, on the other hand, presents a greater dezincification degree. The degradation process extended to a depth of 1 mm, both in the shank and the head.

Apart from dark oxides surrounding phase α, cracks crossing the sample and a high degree of porosity can be observed, also at the shank and the head.

Fig. 9 shows two micrographies of the unetched tack, at two areas of the shank: a) close to the edge; b) at the centre

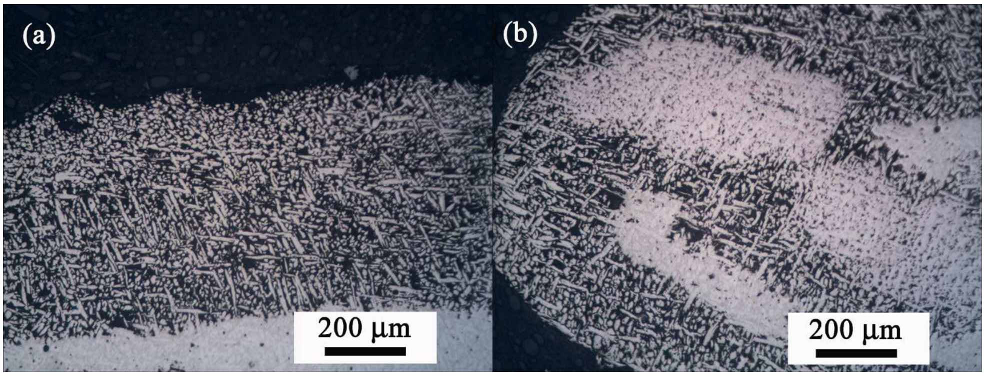

Figure 8 – MT-1a microstructure, as polished, in the following áreas: a) shank perimeter; b) tip.

Microhardness of sample MT-1a is of 120 ±10 HV (no significant differences are observed between the head and the shank). This value corresponds to that observed in pieces of similar alloys, hot formed. Ashkenazi et al. (2014) In the case of MT-1b, values the measured on the head (to avoid heavily degraded areas) was in average 141 ±7 HV.

The microstructures of the analyzed tacks revealed the presence of phases α and β, characteristic of this type of alloy, that in each piece present a different distribution and morphology. The latter suggests varying temperatures, times and cooling rates that can be attributed to variations in the manufacturing process. At the head and close to the surface, both samples present a small area with slightly elongated grains, perpendicular to the shank, as can be seen in Fig. 10(a) and Fig. 11(a).

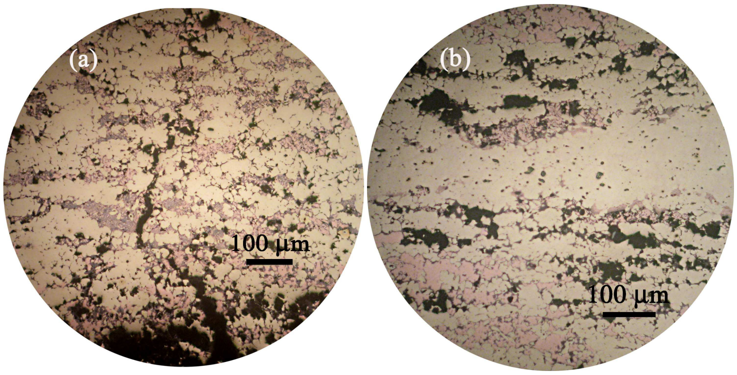

Figure 9 – MT-1b tack photomicrography.As polished

The microstructure observed at the centre of the MT-1a tack's shank, presents β matrix grains and acicular phase α, that grew from large grains of the former. These features are interpreted as a result of a long-lasting heating process at a temperature above 700 ° C - at which the material is in a state β -; then forming by deformation, giving enough time for recrystallization and grain growth to occur, but followed by fast cooling, which generated elongated grains of the new phase (Fig. 10b). Because of this, no traces of plastic deformation from phase β were left, and, as already noted, just a slight deformation of both phases in the head area can be appreciated.

Furthermore, the microstructure of the MT-1b tack presents α phase grains of equiaxed morphology in a clearly oriented β matrix (longitudinal at the shank and transverse at the head). It only exhibits a slight deformation of the α grains at the upper zone of the head, appreciated in the curvature of annealing twins (Fig. 11a). Here, the forming lines converge towards the centre of the piece. In Fig. 12, the aligned microstructure resulting from hot forming is indicated with dotted lines.

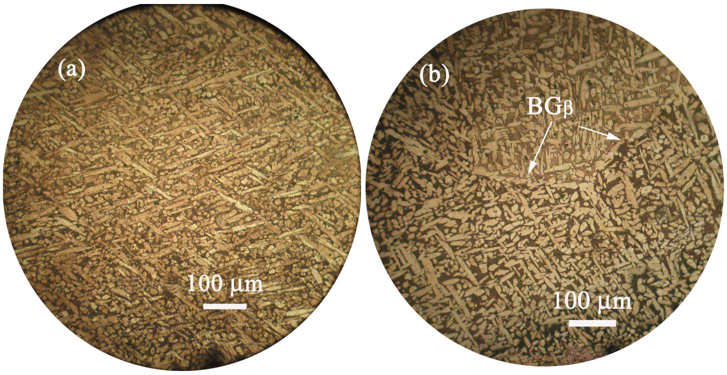

Figure 10 – Microstructure of MT-1a tack, where two phases - α (light) and β (dark) can be appreciated: a) head; b) shank, BG β Grain boundary original β phase. Etchant: HCl $FeCl_3$ aqueous solution.

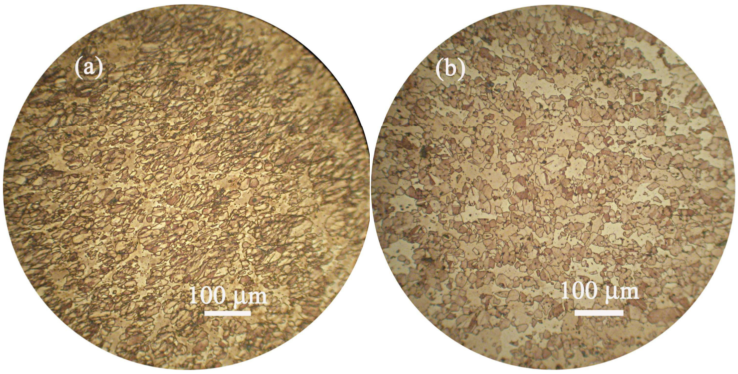

Figure 11 – Microstructure of the MT-1b tack: a) head; b) shank. Etchant: $NH_4OH:H_2O:H_2O_2$

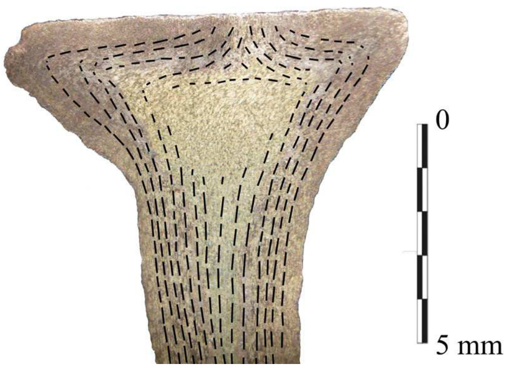

Figure 12 – Longitudinal section of MT-1b tack. The orientation of the microstructure resulting from the forming process is highlighted.

According to what was observed, MT-1b tack presents a microstructure consistent with a hot forming process Considering the orientation and morphology of the shank and head grains, it can be assumed that the manufacturing process consisted in two stages: a) sectioning of the raw material and deformation to conform the shank and head, at a temperature at which the majority of the material remained in state β (an estimate of 700ºC). The degree of deformation, the temperature, and the time it remained there, did not allow for recrystallization to occur. b) Cooling, at a temperature and/or rate that allowed for the formation of equiaxed phase α grain to occur.

The convergence of forming lines towards the top of the head is considered a result of the sectioning of the material while it was at a high temperature. The latter may be indicative of a mechanical manufacturing process similar to that used for the production of iron nails from wire during the 19th century. Nelson (1968). Among the earliest possible alternatives, there is the method of manufacturing by carved rolls (with the nail's shape), patented in 1790 by Thomas Clifford. Martin (1813)

4. Conclusions

This work determined the characteristics of the manufacturing process and the degradation state of the sheathing remains from a shipwreck located at Chubut's seashore. The results, together with historical information as well as from other archaeological sites, allowed to establish an approximate date for the shipwreck. It was determined that the sheet was made in a brass similar to Muntz metal (1832). The piece possesses small quantities of Sn, which may be a product added to enhance the material's resistance to corrosion. The tacks, on the other hand, were manufactured by a hot forming process, most likely mechanical. The alloy used for the sheet , together with the manufacturing method by which the tacks were made, allow to ascribe the technology of the analyzed remains to the 19th Century.

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References

Ashkenazi D., D. Cvikel, A. Stern, S. Klein e Y. Kahanov, 2014. Metallurgical characterization of brass objects from the Akko 1 shipwreck, Israel. Materials Characterization, 92,49-63.

Bingeman J.M, J.P. Bethell, P. Goodwin y A.T. Mack, 2000. Copper and other sheathing in the Royal Navy. The International Journal of Nautical Archaeology, 29 (2),218-229

Campanella L, O. Colacicchi Alessandi, M. Ferretti y S.H. Plattner, 2009. The effect of tin on dezincification of archaeological copper alloys. Corrosion Science, 51,pp.2183.

Ciarlo N.C, M.C. Lucchetta y H. De Rosa, 2013. Análisis metalográfico y químico de un conjunto de artefactos recuperados del naufragio Triunfante (1756-1795), Golfo de Rosas (Cataluña, España). El vaixell Triunfante: Una fita de la ciència i de la tècnica del segle XVIII (X. Nieto, M. Pujol y G. Vivar, eds.). Girona, España: Museu d'Arqueologia de Catalunya,175-188.

Davies D.D. (ed.), 1993 . A Note on the dezincification of brass and the inhibiting effect of elemental addictions. New York: Copper Development Association Inc.,1-9.

Jones T.N., 2004. The Mica Shipwreck: Deepwater Nautical Archaeology in the Gulf of Mexico. Thesis for the degree of Master of Arts, Texas A&M University. Texas, EE.UU.: Ms

Lorusso H., H.G. Svoboda y H. De Rosa. 2003. Caracterización microestructural de componentes metálicos hallados en el pecio de Reta. Jornadas SAM/CONAMET. Bariloche, Río Negro,1103-1106.

Martin T., 1813. Nail-making. The Circle of the Mechanical Arts; Containing Practical Treatises on the Various Manual Arts, Trades, and Manufactures. Londres: Richard Rees,pp.454-457

Nelson L.H., 1968. Nail chronology as an aid to dating old buildings. American Association for State and Local History Technical Leaflet 48, History News, 24 (11).

Ozgowicz W., E. Kalinowska-Ozgowics, B. Grzegorczyk, 2010, The microstructure and mechanical properties of the alloy CuZn30 after recrystallization annealing. Journal of Achievements in Materials and Manufacturing Engineering, 40,:15

Polan W., 1992. Corrosion of copper and copper alloys. ASM Handbook, 13, 9na. ed. EE.UU.: ASM International,pp.1507.

Schweitzer P.A. 2007. Fundamentals of Metallic Corrosion: Atmospherics and Media corrosion of metals. Corrosion Engineering Handbook. Florida, EE.UU.: CRC Press Taylor. Francis Group, 2nd. ed

Staniforth M., 1985.The introduction and use of Copper Sheathing – A history. The Bulletin of the Australian Institute for Maritime Archaeology, 9 (1-2),21-48.

Stoffyn-Egli P., D.E. Buckley and J.A. Clyburne,1998. Corrosion of brass in a marine environment: mineral products and their relationship to variable oxidation and reduction conditions. Applied Geochemistry, 13,pp643.